

Undercooling Limits and Thermophysical Properties in Glass Forming Alloys

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Objectives of the Research

The primary objective of this program is to produce deeply undercooled metallic liquids and to identify factors that limit undercooling and glass formation. The main research objectives are:

- (i) Investigating undercooling limits in glass-forming alloys and identifying factors that affect undercooling.
- (ii) Measuring thermophysical properties and investigating the validity of the classical nucleation theory and other existing theories in the extreme undercooled states.
- (iii) To investigate the limits of electrostatic levitation technology in the ground base and to identify thermophysical parameters that might require reduced-g environment.

Relation to the Gravitational Field

When experiments are conducted in a 1-g environment, all gravity caused effects such as convective flows, sedimentation and buoyancy still remain in the levitated melts. In addition, large forces that are needed to levitate a sample against gravity can cause flows in the melts. The High Temperature Electrostatic Levitator (HTESL) is a relatively recent development. Its limitations in 1-g conditions have not been fully established. Although considerably less flows are expected with electrostatic levitation, very little is known about flows induced by the electrostatic forces. The most seriously affected transport properties might be atomic diffusion, viscosity, and thermal conductivity. In this ground base program, we will identify the thermophysical properties and their temperature ranges which require reduced-g condition for their measurements.

Progress of the Research

(A) Thermophysical properties of Ni-Zr alloys (NiZr , NiZr_2 , $\text{Ni}_{36}\text{Zr}_{64}$ and $\text{Ni}_{24}\text{Zr}_{76}$) have been extensively measured in order to investigate their alloying effect on the undercooling level and the glass formability. Properties measured were specific volume, surface tension, viscosity, and the ratio between the specific heat to the hemispherical total emissivity. What we were interested in was the effect caused by the presence of chemical short-range order (formation of the associated species) which existed in some compound forming liquid alloys.

We used the HTESL at JPL[1] to isolate samples from the contamination associated with containers and to process in a high vacuum environment, which assured consistent and repeatable undercooling levels. We selected Ni-Zr alloys, NiZr and NiZr_2 are compound forming alloys, and $\text{Ni}_{36}\text{Zr}_{64}$ and $\text{Ni}_{24}\text{Zr}_{76}$ are eutectic alloys. For the identification of associated species in the alloys, we measured specific volumes and viscosities of these alloys.

Figure 1 shows the specific volumes of the four alloys as a function of decreasing temperature. The melting point of each alloy is indicated by the arrow. Note that the specific volume of the NiZr₂ alloy is significantly smaller than those of the other alloys. Figure 2 shows the viscosity of the alloys as a function of temperature. Note that the viscosity of the compound-forming alloys are higher than those of the eutectic alloys even at temperatures well above the melting point. Table 1 shows the undercooling level, $\Delta T = T_m - T_N$, where T_m is the melting point (or eutectic temperature) and T_N is the nucleation temperature of the alloys. As a reference, the undercooling levels of the metals are also shown. Note that the undercooling level of NiZr₂ is smaller than those of other alloys.

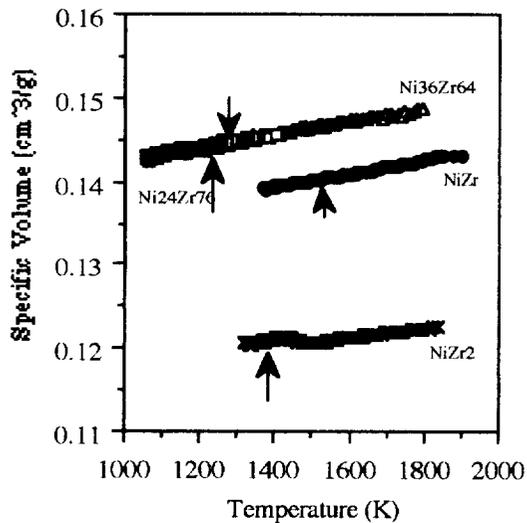


Fig. 1. Specific volume of Ni-Zr alloys

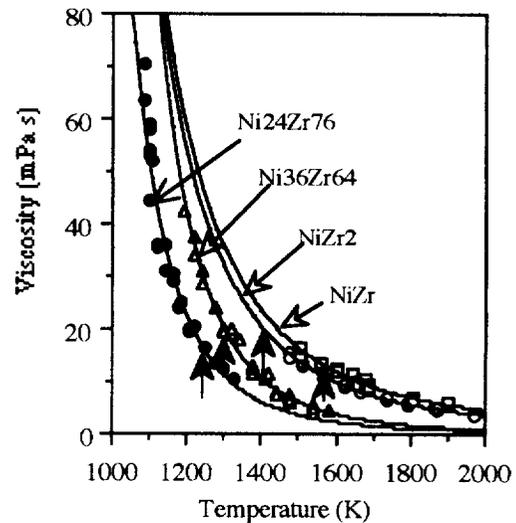


Fig. 2. Viscosity of Ni-Zr alloys

These specific volume data indicate the presence of associated species in the form of NiZr₂. On the other hand, the viscosity data indicate the presence of both NiZr and NiZr₂. As seen in Table 1, the NiZr₂ alloy shows significantly small undercooling compared with those of other alloys and the metals. This difference should not have arisen from the experimental conditions because the sample preparation and the experimental procedure are the same for all of the alloys. Since the NiZr₂ liquid alloy possesses a specific volume which is comparable to that of the compound solid, it is likely that the bonding of the species is very similar to that of the compound solid including the lattice parameters. If this is true, a drastic local structural rearrangement is not required when the liquid is transformed into the solid.

Table 1. Undercooling Level, ΔT of the alloys and metals.

Metal or Alloy	Ni	NiZr	Ni ₃₆ Zr ₆₄	NiZr ₂	Ni ₂₄ Zr ₇₆	Zr
T_m or T_E (K)	1728	1533	1283	1393	1233	2130
$\Delta T/T_m$ (%)	14	11	17	6	14	15

According to classical nucleation theory, the nucleation rate, I , is given by the following form

$$I \sim \exp\left(-\frac{\sigma_{sl}^3}{\Delta G^2}\right) \quad (1)$$

where σ_{sl} and ΔG are the liquid/solid interfacial energy and the free energy difference between the solid and liquid, respectively. Since σ_{sl} is always positive, it acts as a barrier for nucleation. The larger the σ_{sl} value, the more resistant the liquid is to nucleation, which results in a large undercooling level prior to the onset of crystallization. As is assumed above, if the NiZr_2 liquid has a similar local structure to the solid, distortions should be small when the two phases contact to form the interface. As a result, the interface has a small interfacial energy. Thus, the small undercooling of the NiZr_2 alloy can be attributed to the small interfacial energy.

Rotating Molten Metallic Drops and a New Way of Measuring Surface Tension

A new technique which is capable of systematically inducing rotation on a levitated metallic drop was developed to study the dynamics of rotating charged metallic drops and to verify a new approach for measuring the surface tension.

Molten aluminum and tin drops were levitated in a high vacuum by controlling applied electric fields, and they were systematically rotated by applying a rotating magnetic field. As the drops gradually (or step by step) gained angular momentum from their static states, their shapes evolved along an axi-symmetric branch until a bifurcation point was reached at which point in time, transformation from the axi-symmetric to tri-axial shape took place. With an assumption of "effective surface tension", which includes the effect of reduced surface tension due to the surface charges, the results agreed quantitatively well with the Brown and Scriven's prediction [2]. The normalized rotation frequencies at the bifurcation point agreed well with the predicted value, 0.559, within 2%.

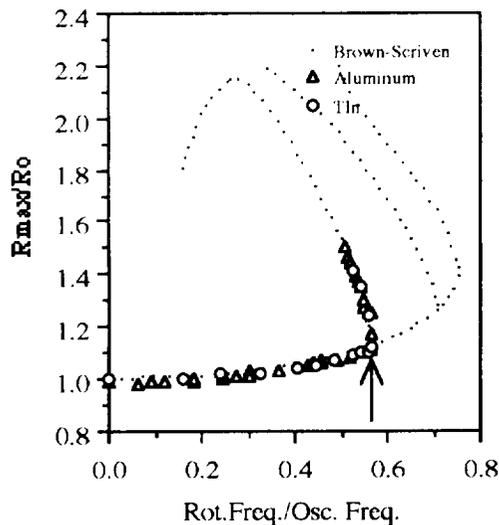


Fig. 3. Distortion vs. rotational rate

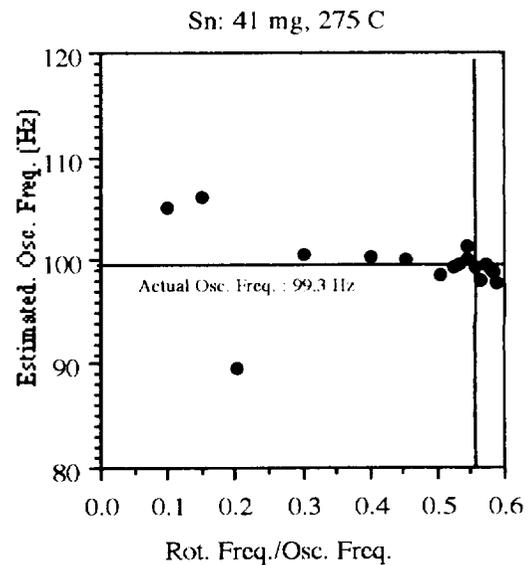


Fig.4. Effective osc. freq. vs. rot. rate

Once agreement with the theory was confirmed, we attempted to use it to explore an alternative way of measuring surface tension. This approach of measuring surface tension using drop

rotation was proposed earlier by Elleman et al.[3]. For low viscosity liquids, measuring the resonant oscillation of a levitated drop is an accurate means of extracting its surface tension[4, 5]. However, for high viscosity liquids where drop oscillations cannot be induced, a new non-contact technique is needed. For example, viscosity of glass forming alloy liquids increase nearly 14 orders magnitude before their glass transition temperatures are reached. The solution to finding an alternate method for surface tension measurement can be found from Fig. 3. If a drop rotates according to the theoretical curve as shown in Fig. 3, one can determine the effective oscillation frequency at any point of the curve if the shape parameter (R_{max}/R_0) and the corresponding drop rotation frequency are known. Since the drop rotation frequency of an axi-symmetric drop is difficult to measure if the drop surface is extremely uniform, measurements of the drop rotation frequencies should be made on the triaxial branch close to the bifurcation point. Since $\omega_{rot}/\omega_{osc} = 0.559$ at the bifurcation point, and the rotation frequency can be measured, the effective oscillation frequency can be determined. Fig.4 demonstrates how effective oscillation frequency of a molten tin drop approaches actual oscillation frequency as the rotation frequency approached the bifurcation point. This approach to the surface tension measurement should be applicable to homogeneous metallic melts of broad viscosity ranges as long as the solid-body rotation condition is satisfied.

Measurement of Surface Tension of Viscosity of a Viscous Glassforming Alloy
 $(Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5})$

We have attempted a preliminary demonstration of surface tension measurement using the rotation method described above. We chose a bulk glassforming alloy ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$) which was provided earlier by the Caltech's William Johnson's group. Initially the sample was heated to $\sim 250K$ above the melting temperature in order to ensure that the drop oscillation could be induced in response to an applied oscillating electric field. Observed oscillations were exponentially decaying transient signals, and they were axi-symmetric $P_2(\cos\theta)$ mode. The surface tension was extracted from the drop oscillation frequency and the viscosity was calculated from the time constant of the transient oscillation [5]. As this process was continued with the temperature lowered a step at a time, we soon hit a limiting temperature below which we could not induce the oscillation within the capability of the instrument. When the rotation method for measuring surface tension was

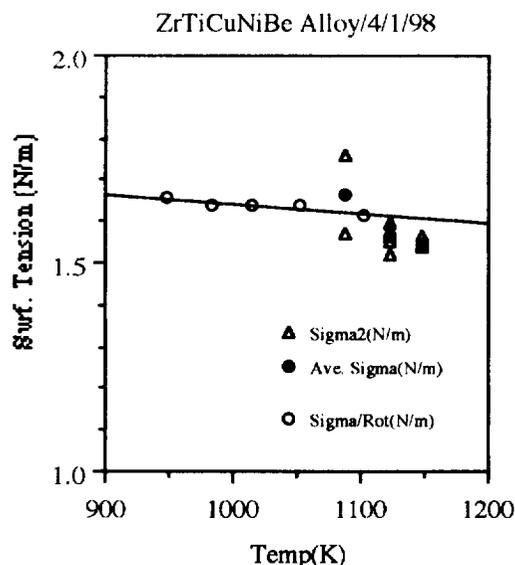


Fig. 5 Surf. tension of a bulk glassforming alloy.

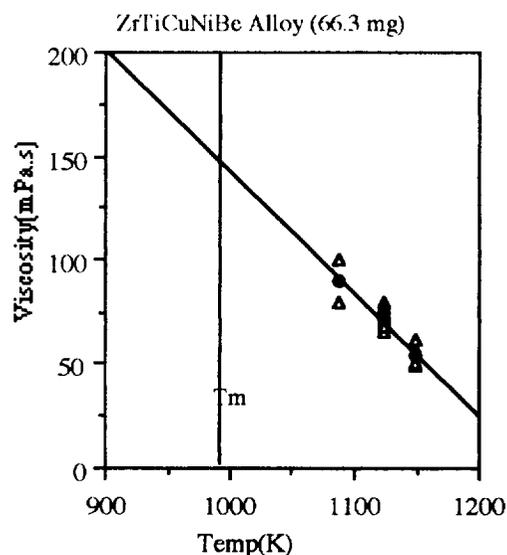


Fig. 6. Viscosity of the same alloy.

applied, we could measure the surface tension to much lower temperature as shown in Fig. 5 by open circles. Also superimposed in Fig. 5 are the surface tension data which were obtained by the transient drop oscillation method. One can observe that the uncertainty in surface tension increases rapidly with the lowered temperature. Fig. 6 shows the viscosity data obtained from the same transient oscillation signals. We noticed that the uncertainty in viscosity data does not increase nearly as rapidly as the surface tension data with lowered temperature. We also noted that the viscosity at the melting temperature is expected to be as high as 150 mPs. To our knowledge, viscosity measuring method based on the sample rotation does not exist at this time. However, its development may be possible.

A New Non-Contact Technique for Measuring Electrical (and Thermal) Conductivity[6]

Electrical conductivity is one of the most sensitive indicators of changes in the nature of chemical binding. In general, electrical conductivity is proportional to carrier density and carrier mobility. A change in the nature of the chemical binding primarily alters the carrier density, and the structural changes alter carrier mobility. Very early investigations of metals showed that the conductivity decreased approximately by a factor 2 at the melting point, while it increased in silicon and germanium as they transform from semiconducting solids to conducting liquids. The electrical conductivities of metallic liquids are of obvious importance to many liquid processing operations (e.g. electric furnace steel making and refining operations, electromagnetic stirring for melt cleanliness and microstructural control) and it is a sensitive measure for concentration fluctuation in a critically mixed liquid alloy near the critical point in the homogeneous liquid phase. The high electrical and thermal conductivity of metals in their condensed states can be attributed almost entirely to freely moving electrons, or conduction electrons. From the metallurgical point of view, relatively few studies have been carried out on the electrical properties of liquid metals and alloys. Thermal conductivity is also of significance in liquid metal processing operations.

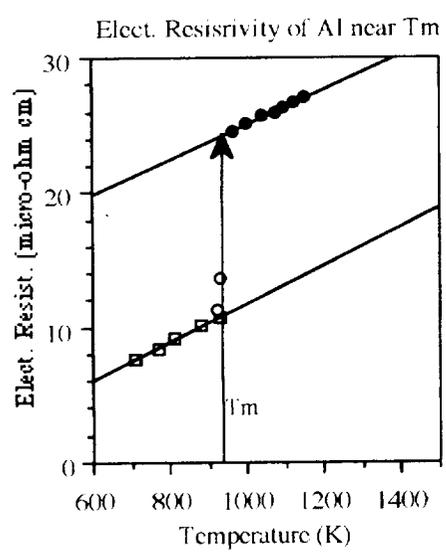


Fig. 9. Electrical resistivity if aluminum.

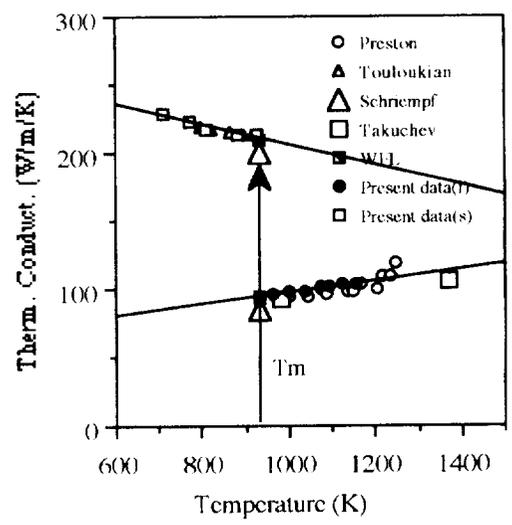


Fig. 10. Thermal conductivity determined by W-F-L Law using the data from fig. 9.

We have developed a non-contact electrical conductivity measurement technique that was adapted to the high temperature electrostatic levitator (HTESL). A rotating magnetic field was applied to a levitated drop, and the induced torque was measured. According to the theory of

induction motors, induced torque should be proportional to the electrical conductivity of the liquid drop. , As it stands now, this technique measures the relative changes of electrical conductivity (or resistivity), therefore, it requires a reference point for calibration. Fig. 7 shows the electrical resistivity of aluminum around the melting temperature.

Accurately measuring thermal conductivity of molten metals is usually more difficult than the measurement of electrical conductivity. Inaccuracies in directly measured thermal conductivity are primarily caused by the difficulties in accurate heat flow measurements, and also to a certain degree, by flows taking place in a melt. However, if thermal and electric conduction take place primarily by free electrons, these two conductivity should be connected through the Wiedemann-Franz-Lorenz Law. Using this law may allow us to obtain more accurate values for thermal conductivity from accurately measured electrical conductivity. Fig. 8 shows the thermal conductivity so determined for aluminum around the melting temperature. Our results agree quite well with independently measured thermal conductivity given by the literature.

Upgrading the JPL HTESL

Upgrading effort of the JPL HTESL facility is essentially complete. The old HTESL did not have true temperature measuring capabilities. Thermophysical properties are usually measured as a function of temperature. However, without knowing true temperature, measured properties cannot be considered credible. The spectral emissivity measurements, laser heating and sample rotation capabilities are three important additions to the new HTESL. Operation of a 100 watt YAG laser was successfully tested by repeating the melting-freezing cycle of a metallic alloy. The sample rotation capability has been thoroughly tested using various solid and molten materials. In summary, the new facility can measure the following properties:

- (1) true temperature by measuring spectral emissivity,
- (2) density (or the volume expansion coefficient),
- (3) the ratio between the specific heat and the hemispherical total emissivity,
- (4) surface tension of liquids within a wide viscosity range,
- (5) viscosity,
- (6) electrical conductivity.
- (7) thermal conductivity determined from measured electrical conductivity using the Wiedemann-Franz-Lorenz Law.

References:

- [1] W. K. Rhim, S. K. Chung, D. Barber, K. F. Man, G. Gutt, A. Rulison, and R. E. Spjut: "An Electrostatic Levitator for High Temperature Containerless Materials Processing in 1-g," Rev. Sci. Instrum. 64: 2961, 1993.
- [2] R. A. Brown and L. E. Scriven, "The Shape and Stability of Rotating Liquid Drops," Proc. R. Soc. Lond. A 371, 331, 1980.
- [3] D. D. Elleman, T. G. Wang, and M. Barmatz: "Acoustic Containerless Experiment System: A Non-Contact Surface Tension Measurement," NASA Tech. Memo. 4069, Vol. 2, 557, 1988.
- [4] W-K. Rhim, S.K. Chung, and D.D. Elleman, "Experiments on Rotating Charged Liquid Drops," Proc. 3rd International Colloquium on Drops and Bubbles (ed. T. G. Wang), AIP Conf. Proc. 197: 91, 1988 .
- [5] W. K. Rhim, K. Ohsaka, and R. E. Spjut, "A non-contact technique of measuring surface tension and viscosity of molten materials using high temperature electrostatic levitator," Rev. Sci. Instrum. (accepted).
- [6] W. K. Rhim and T. Ishikawa: "Non-Contact Electrical Conductivity Measurement Technique for Molten Metals", Rev. Sci. Instrum. (accepted)